



Long-range catalytic hydrodechlorination of preadsorbed DDT at ambient temperature

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ABSTRACT

Reductive catalytic conversion of DDT (p,p'-dichlorodiphenyltrichloroethane) was studied under ambient conditions in a hydrogen atmosphere using platinum and palladium deposited on several supports, in particular on porous alumina and silica. Almost complete hydrodechlorination and hydrogenation of DDT and its dehydrochlorination byproduct DDE (p,p'-dichlorodiphenyldichloroethene), leading to the formation of diphenylethane (with Pd) and dicyclohexylethane (with Pt), were observed at ambient temperature within minutes or hours. Rapid hydrodechlorination also takes place after depositing DDT and the metal component on separate particles and mixing them mechanically. This long-range reactivity can be explained either by a fast surface diffusion of DDT or DDE, or by hydrogen spillover. Irrespective of the mechanism, the reactivity thus bridges the barrier across solid particle interfaces. Most findings indicate the fast diffusion of target compounds as dominant mechanism for the observed long-range reactivity.

1. Introduction

The long-range interaction in catalytic systems allows the interaction of reactants and sites over distances in the micrometer or even millimeter and centimeter range. Prominent examples are not only the bifunctional catalysis in the conversion of hydrocarbons on catalysts with acidic and hydrogenation/dehydrogenation functions [1–3] but also spillover and remote control mechanisms described for activated hydrogen [4–6] and oxygen [6] as reacting species. In both cases, reactants or intermediates are able to diffuse over macroscopic distances, which is an ongoing subject of research, especially with respect to the nature and stability of activated species [5–9]. In this study, long-range catalytic conversion is considered in the context of the decontamination of solid materials containing halogenated pollutants. In contrast to many other studies in this field on treatment in aqueous or solvent phases, this investigation is focused on the direct dechlorination on solid materials in contact with a H₂-containing gas phase under mild reaction conditions, namely ambient temperature and pressure.

Awareness of toxicity and cancerous risks of organochlorine biocides [10–12] led to the search for remediation methods for contaminated media. In particular, DDT (p,p'-dichlorodiphenyltrichloroethane) has a

prominent relevance because it was widely used as biocide against insects and other pests after about 1940, until it was widely banned beginning in the 1970s and finally in the Stockholm Convention [12–14]. After decades of almost non-critical use as “miracle weapon”, a more differentiated view evolved when an accumulation of DDT was found in animal and human fat tissue as well as in the environment [15, 16].

An established method for DDT destruction is high-temperature incineration, which is, however, energy-intensive and associated with the loss of the treated material. Oxidation at lower temperature has an inherent risk of incomplete oxidation and thus the formation of highly toxic partially oxidized products such as polychlorodibenzodioxins or -furans [17,18]. Additionally, the presence of pollutants embedded in an organic matrix leads to a high consumption of oxidants (e.g. of ozone or hydroxyl radicals) and a variety of undesired side reactions.

The reductive hydrodechlorination (HDC) of DDT and other similar compounds such as p,p'-dichlorodiphenyldichloroethene (DDE) and p,p'-dichlorodiphenyldichloroethane (DDD) usually leads to a substitution of one or more chlorine atoms by hydrogen without changing the carbon skeleton. DDE is formed from DDT by a dehydrochlorination (DHC) reaction also occurring in natural environments [19].

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Most previous studies investigate the conversion in aqueous or organic phases; the results potentially relevant for this study can be summarized as follows. Due to the very low water solubility of DDT (about $5 \mu\text{g L}^{-1}$ at 20°C [20]), organic co-solvents have been often used [21].

Zero-valent iron (ZVI, Fe^0) is an established agent for dechlorination reactions in water remediation [22]. It is an efficient reductant of hazardous chemicals such as chlorinated methanes and ethenes [23]. It is, however, much less or even not active for the degradation of chlorinated aromatic compounds such as chlorobenzene [24] as well as for some aliphatic compounds such as dichloromethane and 1,2-dichloroethane [25].

Many studies on ZVI [26 and references therein] show that removal of chlorine bound to polychlorinated aliphatic carbons is much faster than that of chlorine bound to aromatic carbon. Discussing the reaction scheme for ZVI with DDT as educt, Tian et al. [27] postulated two reaction pathways: either via electron transfer leading to DDE as main product (DHC), or via a hydrogen transfer yielding DDD (HDC). In a recent study, Kopinke et al. [26] have provided a detailed literature survey on DDT dechlorination with ZVI, questioning the removal of chlorine bound to aromatic rings and emphasizing the incomplete balance of reaction products, i.e. their 'disappearance', observed in many studies. By comparing experiments with and without the possibility of a direct electron transfer between iron and carbon, they came to the conclusion that hydrogen transfer, e.g. by a spillover process, plays an important role in the dechlorination reaction. In addition to results with pure ZVI as nano- or micro-particles and also with systems combining ZVI with carbon materials for enrichment of hydrophobic organic pollutants [28], further dechlorination with respect to the chlorine in the aliphatic group has been found for bimetallic systems such as Mg^0 -Zn, Mg^0 -Ni and Mg^0 -Co [21,29]. Suresh [21] reviewed reductive remediation of contaminated materials using metals and especially the synergy of corrosive metals (Mg^0 , Zn^0 or Fe^0) with metals catalytically active for hydrogenation (Pd^0 or Ag^0) [21 and references therein].

Keane (2011) has provided a detailed analysis of the literature on the use of supported Pd catalysts for HDC reactions under various temperature and hydrogen pressure conditions [17]. He summarized the advantages of catalytic HDC conversion of chlorinated contaminants in comparison to conventional methods such as phase separation, adsorption (not only on activated carbon but also on waste materials [30]), high-temperature hydrogenolysis [31] or combustion, and also biodegradation, as follows: (i) low-temperature non-destructive transformation without NO_x and SO_x emissions, (ii) avoidance of dioxin or furan formation, (iii) option of selective chlorine removal, (iv) absence of thermally initiated radical reactions, (v) options for batch or flow reaction modes, and (vi) possible use as pretreatment step for detoxification prior to biodegradation. In contrast to studies in aqueous solution or suspensions, literature on dechlorination of chlorinated hydrocarbons and especially DDT under ambient conditions in the gas phase is rare.

Gas-phase HDC has been described for a wide spectrum of aliphatic and aromatic reactants using mainly Pd and Ni as active metals. A variety of solid supports such as carbon, alumina, silica, magnesia have been tested. The selectivity of conversion of polychlorinated organic compounds is often determined by steric constraints [17 and references therein]. A detailed analysis of Pd systems for dechlorination showed that the conversion of aromatic reactants typically necessitated elevated reaction temperatures, usually above 140°C [17]. For this reason, studies on HDC at ambient temperature are relatively rare. High selectivities ($\geq 85\%$) with respect to the fully dechlorinated products were found for chlorobenzene with Pd on activated carbon at 150°C [32], 1, 2-dichlorobenzene using Pd/ Al_2O_3 catalysts at 150°C [33] and 1, 3-dichlorobenzene with a Pd/ SiO_2 catalyst at 150°C [34]. In addition to a role of the support for stabilizing the dispersed metal clusters, Keane (2011) [17] and recently Lei et al. [35] also postulated a possible role of activated hydrogen and H^* spillover in the reaction mechanism. This phenomenon, including an activation of hydrogen on the metal and a

subsequent diffusion as activated H^* to the support, has been described for a variety of supports (e.g. alumina, silica, titania, tungsten oxide, zeolites or carbon), metals (e.g. Pt, Pd, Ru, Rh, Ni) and reactions including hydrogenation, hydrogenolysis and bifunctional catalysis. An overview is provided by several reviews [4–6]. A contribution of H^* spillover to the dechlorination of chlorobenzene and 3-chlorophenol [36] as well as trichlorobenzenes [37] on a Ni/ SiO_2 catalyst has been shown and discussed, in particular the dual nature of spilt-over H^* as electron donor providing both neutral H and H^+ species [5,38,39]. Most studies on HDC catalyzed by transition metals have been carried out at elevated temperatures and with volatile chlorinated hydrocarbons. Although H^* spillover may play a role, gas-phase diffusion is probably the main process leading to the necessary contact between target compounds and catalytically active metals under these conditions.

The situation is different when studying conversion of hardly volatile compounds such as DDT at ambient temperature. Due to the very low vapor pressures of these chlorinated contaminants (e.g. about $25 \mu\text{Pa}$ at 20°C , depending on the source [20]), a migration through the gas phase is expected to be too slow to obtain a significant conversion in acceptable reaction times. In this study, the long-range reactivity of the model compound DDT for dechlorination in hydrogen atmosphere was studied using one- and two-component Pt- or Pd-containing fixed-bed samples. In one-component samples, both DDT and catalytic sites were deposited on the same particle, whereas for two-component samples the DDT- and metal-containing particles were separately prepared and mixed afterwards. Particle sizes in the range of tens to hundreds of micrometers were investigated in this study.

2. Materials and methods

2.1. Chemicals

DDT (purity $> 99.3\%$) and DDE ($> 99.8\%$) were obtained from the Institute of Organic Industrial Chemistry of Poland (Warsaw). Both chemicals can be represented by simplified structure formulas, $[\text{Cl-Ph}]_2>\text{CH-CCl}_3$ and $[\text{Cl-Ph}]_2>\text{C=CCl}_2$. This notation will also be used for the products found in order to better illustrate the reaction pathways (see Table 1).

Phenanthrene- d_{10} (Cambridge Isotope Laboratories) and 4,4'-dichlorobiphenyl (PCB15, Riedel de Haen) were used as internal standard substances in product analysis. The solvents acetone, methanol, chloroform and toluene (p.a., Merck, Darmstadt) were applied for sample preparation and extraction as described in detail later. Unless stated otherwise, all chemicals were used as obtained without further purification.

All gases (hydrogen, nitrogen, helium) used were of high purity ($> 99.999\%$).

2.2. Metal oxides and catalysts

The study was focused on the porous oxide materials $\gamma\text{-Al}_2\text{O}_3$ and silica gel. As a reference hydrophobic carrier material, activated carbon (AC) was tested.

As catalytically active metals, palladium and platinum were studied.

A summary of the oxides and catalysts with their main properties is given in Tables 2 and 3, respectively. The materials were obtained from various providers and used as provided.

The specific surface areas S_{BET} were determined by N_2 low-temperature adsorption using the BET model for evaluation. The metal dispersions were measured applying a standard flow CO chemisorption procedure assuming 1:1 adsorption stoichiometry for surface atoms.

For experiments with crystalline DDT and $\mu\text{-Pd}$, both substances were mixed thoroughly with $\alpha\text{-Al}_2\text{O}_3$ powder using mortar and pestle, resulting in mass fractions of 1 wt.-% each for DDT and $\mu\text{-Pd}$.

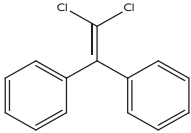
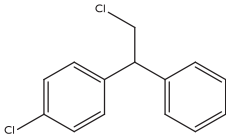
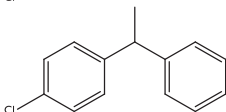
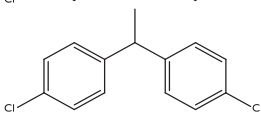
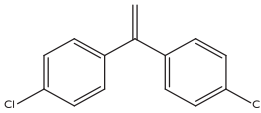
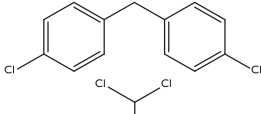
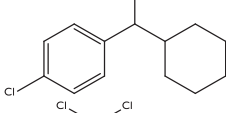
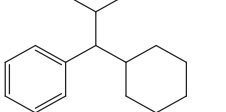
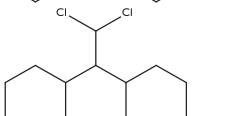
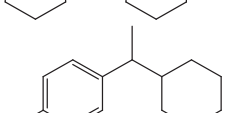
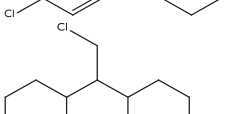
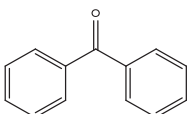
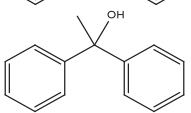
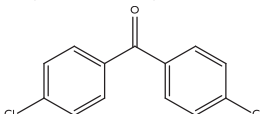
Table 1

Overview of educts, products, abbreviations used and simplified formulas.

Compound name	Formula	Structural formula*	Abbreviation	Simplified structural formula* *
Educts				
Dichlorodiphenyltrichloroethane	C ₁₄ H ₉ Cl ₅		DDT	[Cl-Ph] ₂ >CH-CCl ₃
Dichlorodiphenyldichloroethene	C ₁₄ H ₈ Cl ₄		DDE	[Cl-Ph] ₂ >C=CCl ₂
Fully dechlorinated products				
Diphenylethane	C ₁₄ H ₁₄			Ph ₂ >CH-CH ₃
Diphenylmethane	C ₁₃ H ₁₂			Ph ₂ >CH ₂
Diphenylethene	C ₁₄ H ₁₂			Ph ₂ >C=CH ₂
Phenylcyclohexylethane	C ₁₄ H ₂₀			[Ph, Cy]>CH-CH ₃
Dicyclohexylethane	C ₁₄ H ₂₆			Cy ₂ >CH-CH ₃
Partially dechlorinated products				
Chlorodiphenyl-trichloroethane	C ₁₄ H ₁₀ Cl ₄			[[Cl-Ph], Ph]>CH-CCl ₃
Dichlorodiphenyl-dichloroethane	C ₁₄ H ₁₀ Cl ₄		DDD	[Cl-Ph] ₂ >CH-CHCl ₂
Chlorodiphenyl-dichloroethane	C ₁₄ H ₁₁ Cl ₃			[[Cl-Ph], Ph]>CH-CHCl ₂
Dichlorodiphenyl-monochloroethane	C ₁₄ H ₁₁ Cl ₃		DDMS	[Cl-Ph] ₂ >CH-CH ₂ Cl
Dichlorodiphenyl-monochloroethene	C ₁₄ H ₉ Cl ₃		DDMU	[Cl-Ph] ₂ >C=CHCl
Diphenyldichloroethane	C ₁₄ H ₁₂ Cl ₂			Ph ₂ >CH-CHCl ₂

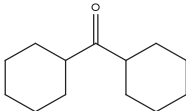
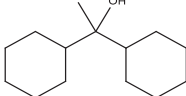
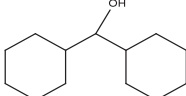
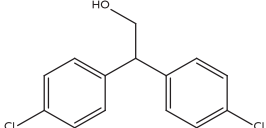
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Table 1 (continued)

Compound name	Formula	Structural formula*	Abbreviation	$\text{Ph}_2 > \text{C} = \text{CCl}_2$ Simplified structural formula* *
Diphenyldichloroethene	$\text{C}_{14}\text{H}_{10}\text{Cl}_2$			
Chlorodiphenyl-monochloroethane	$\text{C}_{14}\text{H}_{12}\text{Cl}_2$		DDMS	$[(\text{Cl-Ph}), \text{Ph}] > \text{CH-CH}_2\text{Cl}$
Chlorodiphenylethane	$\text{C}_{14}\text{H}_{13}\text{Cl}$			$[(\text{Cl-Ph}), \text{Ph}] > \text{CH-CH}_3$
Dichlorodiphenylethane	$\text{C}_{14}\text{H}_{12}\text{Cl}_2$		DDNS (DD0)	$[(\text{Cl-Ph})_2] > \text{CH-CH}_3$
Dichlorodiphenylethene	$\text{C}_{14}\text{H}_{10}\text{Cl}_2$			$[(\text{Cl-Ph})_2] > \text{C}=\text{CH}_2$
Dichlorodiphenylmethane	$\text{C}_{13}\text{H}_{10}\text{Cl}_2$		DDM	$[(\text{Cl-Ph})_2] > \text{CH}_2$
Chlorophenylcyclohexyl-dichloroethane	$\text{C}_{14}\text{H}_{17}\text{Cl}_3$			$[(\text{Cl-Ph}), \text{Cy}] > \text{CH-CHCl}_2$
Phenylcyclohexyl-dichloroethane	$\text{C}_{14}\text{H}_{18}\text{Cl}_2$			$[\text{Ph}, \text{Cy}] > \text{CH-CHCl}_2$
Dicyclohexyldichloro-ethane	$\text{C}_{14}\text{H}_{24}\text{Cl}_2$			$\text{Cy}_2 > \text{CH-CHCl}_2$
Chlorophenyl-cyclohexylethane	$\text{C}_{14}\text{H}_{19}\text{Cl}$			$[(\text{Cl-Ph}), \text{Cy}] > \text{CH-CH}_3$
Dicyclohexyl-monochloroethane	$\text{C}_{14}\text{H}_{25}\text{Cl}$			$\text{Cy}_2 > \text{CH-CH}_2\text{Cl}$
Partially oxidized products				
Benzophenone	$\text{C}_{13}\text{H}_{10}\text{O}$			$\text{Ph}_2 > \text{C}=\text{O}$
Diphenylethanol	$\text{C}_{14}\text{H}_{14}\text{O}$			$\text{Ph}_2 > \text{C}(\text{OH})-\text{CH}_3$
Dichlorodiphenylmethanal	$\text{C}_{13}\text{H}_8\text{Cl}_2\text{O}$			$[(\text{Cl-Ph})_2] > \text{C}=\text{O}$

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Table 1 (continued)

Compound name	Formula	Structural formula*	Abbreviation	$\text{Cy}_2 > \text{C}=\text{O}$ Simplified structural formula* *
Dicyclohexylmethanal	$\text{C}_{13}\text{H}_{22}\text{O}$			
Dicyclohexylethanol	$\text{C}_{14}\text{H}_{26}\text{O}$			$\text{Cy}_2 > \text{C}(\text{OH})-\text{CH}_3$
Dicyclohexylmethanol	$\text{C}_{13}\text{H}_{24}\text{O}$			$\text{Cy}_2 > \text{CH}(\text{OH})$
Dichlorodiphenylethanol	$\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{O}$		DDOH	$[\text{Cl}-\text{Ph}]_2 > \text{CH}-\text{CH}_2(\text{OH})$

*For clarity, isomers and exact nomenclature according to IUPAC are not given here.

* Ph ... phenyl, Cy ... cyclohexyl

Table 2

Overview of oxides and catalysts used, together with their provider and main properties (specific surface area S_{BET} , applied grain size fractions and initial water contents after storage; n.a. – not analyzed).

Name	Description, Nomenclature of the provider	Provider	S_{BET} $\text{m}^2 \text{g}^{-1}$	Grain size fraction μm	Water content wt.-%
$\gamma\text{-Al}_2\text{O}_3$ -A	$\gamma\text{-Al}_2\text{O}_3$ (97.7% purity)	ABCR	185	< 100; 45–100	6.1
$\gamma\text{-Al}_2\text{O}_3$ -B	$\gamma\text{-Al}_2\text{O}_3$, granules, desiccant	Merck	304	45–100; 100–160; 160–250	5.9
$\alpha\text{-Al}_2\text{O}_3$	Aluminum oxide fused, 100 + 200 mesh	Aldrich	< 0.3	50–74	n.a.
SiO_2	Silica gel, Silikagel 60	Merck	490	45–100	5.1
Pd-C	0.5 wt.-% Pd/ $\gamma\text{-Al}_2\text{O}_3$, Eggshell catalyst (G-133 D)	Commercial	137	< 100; 45–100	7.4
Pd-D	1 wt.-% Pd on $\gamma\text{-Al}_2\text{O}_3$	Aldrich	196	45–100	8.6
Pd-E	5 wt.-% Pd on $\gamma\text{-Al}_2\text{O}_3$	Aldrich	96	45–100	3.5
Pt-F	1 wt.-% Pt on $\gamma\text{-Al}_2\text{O}_3$	Aldrich	156	45–100	4.4
Pt-G	5 wt.-% Pt on $\gamma\text{-Al}_2\text{O}_3$	Aldrich	95	45–100	5.3
Pt-H	5 wt.-% Pt on $\gamma\text{-Al}_2\text{O}_3$	Merck	105	45–100	1.6
Pd-K	5 wt.-% Pd on silica gel	ABCR	192	45–100	5.0
Pt-L	1 wt.-% Pt on silica gel	Aldrich	257	45–100	3.7
Pt-M	5 wt.-% Pt on silica gel	ABCR	196	45–100	3.8
$\mu\text{-Pd}$	Pd micro-particles (purity > 99.9%)	ChemPur	n.a.	1.2–2.5	n.a.
Pd-AC	10 wt.-% Pd on activated carbon (AC)	Merck-Schuchardt	943	45–100	7.8

Table 3

Main properties of catalysts applied (metal type and content, metal dispersion, type of support, number of metal atoms per gram catalyst and calculated distance between the metal clusters d_{cluster} using an fcc-based model [40]).

Name	Metal	Metal content wt.-%	Dispersion %	Support	Metal density 10^{19} atoms $\text{g}^{-1} \text{cat}$	Distance nm
Pd-C	Pd	0.5	18	$\gamma\text{-Al}_2\text{O}_3$	2.8	178
Pd-D	Pd	1	36	$\gamma\text{-Al}_2\text{O}_3$	5.6	44
Pd-E	Pd	5	24	$\gamma\text{-Al}_2\text{O}_3$	28	31
Pt-F	Pt	1	30	$\gamma\text{-Al}_2\text{O}_3$	3.1	85
Pt-G	Pt	5	18	$\gamma\text{-Al}_2\text{O}_3$	15	63
Pt-H	Pt	5	17.5	$\gamma\text{-Al}_2\text{O}_3$	15	67
Pd-K	Pd	5	5.2	Silica gel	28	552
Pt-L	Pt	1	34	Silica gel	3.1	75
Pt-M	Pt	5	4.4	Silica gel	15	851
Pd-AC	Pd	10	13	Activated carbon	56	143

2.3. Sample impregnation with DDT

Generally, the DDT-impregnated samples were prepared by a wet impregnation method. Solid materials were sieved, and the different grain size fractions were separated. Typically, 5 g of a defined size fraction were mixed with 10–20 mL of acetone containing 25–50 mg of DDT in a 50 mL round-bottom flask, resulting in a theoretical DDT content of 0.5–1 dry wt.-%.

The slurry was mixed thoroughly for 1 h using a horizontal shaker (IKA HS 260 basic) at 250 rpm. The acetone was then removed by means of a rotary evaporator with a bath temperature of 50 °C and a final pressure ≤ 1 mbar. In certain cases, namely for non-porous materials, other DDT contents were achieved by variation of the DDT content in the acetone stock solution.

Before carrying out the catalytic tests, samples were stored under ambient air atmosphere (relative humidity [rF] about 55%), thus reaching an equilibrium moisture content as discussed later.

In most cases, the DDT content was chosen such as to provide a desired incomplete surface coverage. For some metal oxide samples with comparably low porosity, lower DDT contents than mentioned above were used in order to avoid strong DDT agglomeration or even total coverage of the surface. Nevertheless, formation of DDT clusters or

crystals could not be excluded.

For selected samples, the DDT loading was confirmed by means of total organic carbon and chlorine analysis (total oxidation followed by CO₂ and chloride quantification, respectively). All catalytic tests were accompanied by blank measurements, i.e., the analysis of identical reference samples that were not subjected to hydrogen loading. In most cases, at least two parallel samples were analyzed; mean values are presented in the following diagrams.

2.4. Investigation of the dehydrochlorination (DHC) reaction of DDT to DDE on γ -Al₂O₃

The following procedure was used in order to characterize the transformation of DDT during wet impregnation of porous alumina, which will be described later in detail. 8 g of γ -Al₂O₃ granules ($d = 2 \dots 5$ mm) were mixed with 40 mg DDT dissolved in 10 mL acetone in a 50 mL round-bottom flask. The suspension was mixed using a vertical shaker for 2.5 days. The round-bottom flask was then attached to a rotary evaporator and solvent was removed by stepwise reduction of the pressure at 50 °C bath temperature. In time intervals of a few minutes, single granules were taken, extracted and analyzed according to the procedure described below (Section 2.8).

This analysis can be considered as representative not only for the γ -Al₂O₃ support but also for other materials such as ZnO or MgO where a DHC reaction takes place.

2.5. Determination of the water content

The water content of γ -Al₂O₃ and silica gel can be roughly categorized as chemisorbed and physisorbed water, where removal of chemisorbed water can be also described as a condensation of surface hydroxyl groups. In order to avoid this structural modification, heating during the measurement of water contents was limited to a maximum temperature of 250 °C and moisture content was defined as being correlated with water that can be removed up to 250 °C in vacuum (final pressure < 1 Pa).

The measured water contents of porous alumina and silica samples after storage in air under equilibrium conditions were typically in the range of 5–7.5 wt.-%, corresponding in trend to the specific surface areas. These equilibrium values of moisture content generally indicate relatively high, but not complete monolayer coverage for the porous samples when neglecting pore condensation or agglomeration. However, for the non-porous metal oxides including α -Al₂O₃, multilayer coverage has to be assumed, even when considering the lower moisture contents measured gravimetrically.

In a typical HDC experiment with γ -Al₂O₃-A (see Table 2) under a continuous dry purge gas flow (100 mL min⁻¹), the water content continuously decreased from 6.1 wt.-% (initial value) via 5.0 wt.-% (after 30 min), 4.0 wt.-% (60 min), 3.3 wt.-% (90 min) to 3.0 wt.-% after 2 h purge time. Similar results were obtained for silica gel samples. Thus, it can be concluded that during typical experiments with a dry purge gas lasting 2 h, the residual water content was in the range of about 2–4 wt.-%. For lower purge gas flows (25 mL min⁻¹) applied in some experiments, the reduction of moisture content was slower.

This result was confirmed by a temperature-programmed thermal gravimetric analysis (TGA) that will not be described in detail here. A total initial moisture content of 5.7 wt.-% including 3.7 wt.-% of physisorbed and bulk water were determined by means of TGA.

2.6. HDC experiments

The HDC experiments were carried out with one- and two-component samples. For single-component systems, the DDT-impregnated metal catalysts were used alone. For two-component samples, equal amounts (usually 100–300 mg) of DDT-impregnated samples and catalysts were mixed thoroughly. In some cases, other

mass ratios of the two components were used.

The standard experimental procedure for HDC experiments was as follows. As reference, aliquots of the prepared samples were taken before the hydrogen treatment and subjected to solvent extraction followed by gas chromatography/mass spectrometry (GC-MS) and ion chromatography (IC) analysis as described below. The remaining solids mixture was put into a plug-flow fixed-bed tubular glass reactor and purged with gas flows (100 mL min⁻¹): first with N₂ for 15 min, then the reaction was started by changing the gas to H₂. After a defined period of time, the reaction was stopped by changing back to N₂ for 15 min. For post-reaction analysis, aliquots of the fixed bed were taken and subjected to GC-MS and IC analysis. In some experiments, a smaller reactor was used, whereby the gas flows were reduced to 25 mL min⁻¹.

2.7. Characterization of adsorbents and catalysts

The specific surface area was determined on the basis of N₂ adsorption at 77 K with a Belsorb Mini II analyzer (Microtrac BEL, Japan). Before measurement of adsorption isotherms, the powder samples were pretreated by heating up to 250 °C in vacuum with 50 K min⁻¹ until a final pressure below 1 Pa was reached for at least 2 h.

Metal dispersion in the oxide-supported catalysts was determined by means of the CO chemisorption method (10 vol.-% CO in He) with a BELCAT-B device (BEL, Japan). The sample pre-treatment consisted of oxidation in pure oxygen for 15 min and reduction in a hydrogen flow for 15 min at 200 °C. This established procedure does not influence the metal dispersion and is well established for characterizing dispersion in Pt and Pd catalysts (see Table 3).

2.8. Extraction and GC-MS analysis

50–100 mg of the powder samples were extracted with 3 mL of a 1:1 (v/v) mixture of toluene and chloroform containing 30 µg of phenanthrene-d₁₀ or 30 µg of PCB15 as internal standard. The mixture was shaken for 1 h, filtered through a silica plug if necessary in order to remove particulate matter, and directly injected into the GC-MS device.

For GC-MS analysis, a QP 2010 Plus GC-MS (Shimadzu) was used in electron impact ionization mode (70 eV) with a capillary column (5% phenyl-methylpolysiloxane HP 5 MS; length 30 m, inner diameter 0.32 mm, film thickness 0.25 µm). The injection temperature was 230 °C and ion source temperature was 250 °C. The GC oven program was as follows: 40 °C held for 3 min, with a constant heating rate of 10 K min⁻¹ to 250 °C and held for 3 min. 1 µL of sample was injected applying a split ratio of 10:1. Data acquisition was in full-scan or selected ion monitoring modes in the m/z range from 33 to 500 amu. Quantification of components was performed based upon the relative response factors of the individual components to the internal standards phenanthrene-d₁₀ or PCB15. The measured values were corrected with the extraction recovery rates of the analytes.

An overview of the pattern of observed products is given in Table 1. In some experiments, unexpected partially oxidized products such as Ph₂>C(OH)-CH₃, Ph₂>C=O, [Cl-Ph]₂>C=O as well as the further hydrogenated Cy₂>C(OH)-CH₃ and Cy₂>C=O were found. It could be clearly shown in detailed studies that these products were formed during the extraction procedure in the presence of ambient air. They did not appear when the extraction was carried out under pure nitrogen atmosphere or in the absence of Pt or Pd. The two most likely hypotheses are a direct catalytic oxidation on the metal clusters or via H₂O₂ from O₂ and residual chemisorbed hydrogen. Although the oxidation products affect the original HDC product pattern, their yields in the discussed experiments were relatively small (< 10 mol.-% of converted DDT).

2.9. Ion chromatography

For chloride analysis, aqueous suspensions of the samples were produced. In some cases, complete chloride extraction was only

achieved when using slightly alkaline pH values. The aqueous filtrate of the samples was diluted when necessary up to tenfold with deionized (Millipore) water and then subjected to IC analysis with an ICDX 500 system (Dionex). 25 μL of the diluted sample were injected. An anion exchange IonPac AS11-HC column (Dionex) and an ASRS 300 4 mm self-regenerating suppressor were used in combination with an IC-25 conductivity detector. The eluent flow rate was 1 mL min^{-1} with the following gradients of KOH: 7 mM held for 2 min, increase to 8 mM over 6 min, increase to 45 mM over 2 min and then held for 5 min. Reference measurements with the contaminant-free samples were made in order to determine the chloride background value subtracted for quantification of the HDC conversions.

3. Results

3.1. Dehydrochlorination (DHC) of DDT catalyzed by $\gamma\text{-Al}_2\text{O}_3$

For each dechlorination test, a reference sample was extracted and analyzed in parallel in order to characterize the initial content of halogenated hydrocarbons. After the loading procedure, the $\gamma\text{-Al}_2\text{O}_3$ samples contained almost exclusively DDE formed from DDT by DHC reaction, as was verified by chloride analysis (release of one mole chloride per mole transformed DDT). Although the DHC process was not in the focus of this study, it will be shortly considered in order to clarify the starting conditions for the reductive dechlorination itself. Considering the literature [41–43], the DHC reaction can be related to basic sites at the carrier surface, which were not characterized in detail. This explanation is supported by the alkaline pH value of aqueous carrier suspensions (10 wt.-% $\gamma\text{-Al}_2\text{O}_3$), which were 8.7 ($\gamma\text{-Al}_2\text{O}_3\text{-A}$), 9.5 ($\gamma\text{-Al}_2\text{O}_3\text{-B}$) and 8.8 (Pd/ $\gamma\text{-Al}_2\text{O}_3$; Pd-C). In contrast, this DHC reaction was not observable on silica gel after impregnation, i.e., before starting the HDC reaction. This means that DDT was still present on the silica gel surface, whereas DDE was the dominant substrate on $\gamma\text{-Al}_2\text{O}_3$. Storage of loaded silica samples for several days could, however, lead to some DDE formation due to DHC.

It is essential to be aware of the conditions of a transformation of DDT to DDE for the interpretation of experimental results of two-component systems, especially for identification of the reaction sites. Therefore, the conversion of DDT during the impregnation procedure was studied for $\gamma\text{-Al}_2\text{O}_3$ granules and the formation of DDE was detected as a function of time. It was clearly shown that DHC occurs to a large extent already during wet impregnation of the alumina samples and evaporation of the solvent. Results are represented in detail in the Supporting Information part (SI 1).

The formation of DDE from DDT at ambient temperature was also shown independently of the preparation procedure with acetone by mixing silica gel containing 0.5 wt.-% DDT with $\gamma\text{-Al}_2\text{O}_3\text{-A}$. Immediately after mixing, almost no DDE was found in the reference sample, whereas after 60 min, about 15% of the DDT was transformed to DDE, clearly indicating both diffusion of DDT from silica gel to $\gamma\text{-Al}_2\text{O}_3$ and DHC occurring at ambient temperature.

3.2. HDC under ambient conditions in one-component alumina samples

0.5 wt.-% Pd/ $\gamma\text{-Al}_2\text{O}_3$ and 1 wt.-% Pd/ $\gamma\text{-Al}_2\text{O}_3$ samples (Pd-C and Pd-D, respectively) were impregnated with 0.5 wt.-% DDT. DDT was completely transformed into DDE before starting the HDC experiments. This is an indication for a molecularly dispersed rather than crystalline state of DDT and, therefore, a quasi-homogeneous DDT distribution, allowing close contact to the basic sites of the carrier after impregnation. Results with the Pd-C catalyst after 2 h, 4.75 h and 7 h of H_2 treatment are summarized in Table 4. The origin of the significant variation in total recovery rates (usually between 65% and 98%) which was observed in many cases could not be fully clarified. In agreement with literature [45] and references therein, formation of dimers and oligomers which could not be extracted or analyzed by GC-MS could be an explanation.

Table 4

Reaction of DDE (from 0.5 wt.-% DDT) on 0.5 wt.-% Pd/ $\gamma\text{-Al}_2\text{O}_3$ (Pd-C) and on 1 wt.-% Pd/ $\gamma\text{-Al}_2\text{O}_3$ (Pd-D), respectively. As in all following tables, the data are given in mole-% of the products in the sample extracts.

Catalyst	Pd-C				Pd-D	
Reaction time in H_2 / h	0	2	4.75	7	0	2
DDE	100.0	6.8	0.6		100.0	0.1
$\text{Ph}_2\text{>C=O}$		2.0	7.3	0.3		0.9
$\text{Ph}_2\text{>C(OH)-CH}_3$		3.4	3.4	1.2		5.5
$\text{Ph}_2\text{>C=CH}_2$		1.4	4.8	0.4		0.9
$\text{Ph}_2\text{>CH-CH}_3$		81.8	74.0	61.9		79.9
$[\text{Ph,Cy}]>\text{CH-CH}_3$		4.6	9.8	35.0		12.0
$\text{Cy}_2\text{>CH-CH}_3$				1.2		0.8
Recovery rate / %⁺	92	96	116	130	96	130

⁺Amount of carbon extracted from the catalyst sample normalized to the initial carbon loading as DDT

The most notable finding is that a complete dechlorination reaction, including aromatic and aliphatic chlorine substituents with only a small amount of residual DDE, is obtained already after 2 h under ambient conditions with both Pd catalysts. The main product is diphenylethane ($\text{Ph}_2\text{>CH-CH}_3$) formed by complete HDC and hydrogenation of the olefinic double bond. In the further course of the reaction, hydrogenation of the aromatic rings also occurred, resulting in the formation of $[\text{Ph,Cy}]>\text{CH-CH}_3$ and $\text{Cy}_2\text{>CH-CH}_3$. Small amounts of $\text{Ph}_2\text{>C=CH}_2$ and the oxidation products $\text{Ph}_2\text{>C=O}$ and $\text{Ph}_2\text{>C(OH)-CH}_3$ were also found. Chloride yields were found to be 89% after 2 h, 122% after 4.75 h and 100% after 7 h, related to the chlorine content of the initially impregnated DDT.

The observed fast dechlorination reaction was confirmed by another experiment exemplarily illustrated with a commercial Pd/ $\gamma\text{-Al}_2\text{O}_3$ catalyst (Pd-D) exhibiting a homogenous Pd distribution (1 wt.-%, grain size 45–100 μm) impregnated with DDT (0.5 wt.-% target content, determined as 0.46 wt.-% DDE by extraction and GC-MS analysis). As can also be seen in Table 4, all detected substances were completely dechlorinated with the main reaction products $\text{Ph}_2\text{>CH-CH}_3$ (about 80%), $[\text{Ph,Cy}]>\text{CH-CH}_3$ and $\text{Ph}_2\text{>C(OH)-CH}_3$.

Based on the experimental finding that hydrogen treatment of metal-free alumina samples under the same reaction conditions did not lead to any HDC reaction, the catalytic function of Pd is obvious. For the interpretation of the results in Table 4, as well as the Pd contents (0.5 vs. 1 wt.-%), the different metal dispersion for Pd-C (18%) and Pd-D (36%) have to be considered.

A rough estimation of the distance between two metal clusters, assuming a dispersity of 0.3 and hemisphere geometry, leads to values in the range of 30–200 nm for most catalysts with the various metal contents used in this study (see Table 3). Taking into account the size of the DDT or DDE molecules (in the range of 1 nm) and assuming their homogeneous distribution at the surface after wet impregnation, a mobility of the reactants, either of activated hydrogen (H^* , spillover species) or the target molecules (here DDE) has to be postulated (see also Fig. 1 in 3.4.).

In addition to Pd, a second metal, platinum, was tested for the HDC reaction. A Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst (Pt-F, grain size 45–100 μm) was impregnated with DDT (0.4 wt.-%, water content 5.5 wt.-%) and treated at ambient temperature with hydrogen for 2 h. Complete dechlorination and hydrogenation leading to $\text{Cy}_2\text{>CH-CH}_3$ (> 98%) were observed under these conditions. Considering that DDE was the only educt in this reaction after DDT impregnation, not only a complete release of aromatic and olefinic Cl substituents but also hydrogenation of olefinic as well as aromatic structures were observed (compare Table 1).

There is a clear difference in selectivity between Pd and Pt as active metals. Pt is much more active in hydrogenation of aromatic rings. Such different product patterns would probably not be expected for spilt-over hydrogen H^* as migrating species [4–6], because the spilt-over hydrogen H^* meets the same target molecule on the same carrier

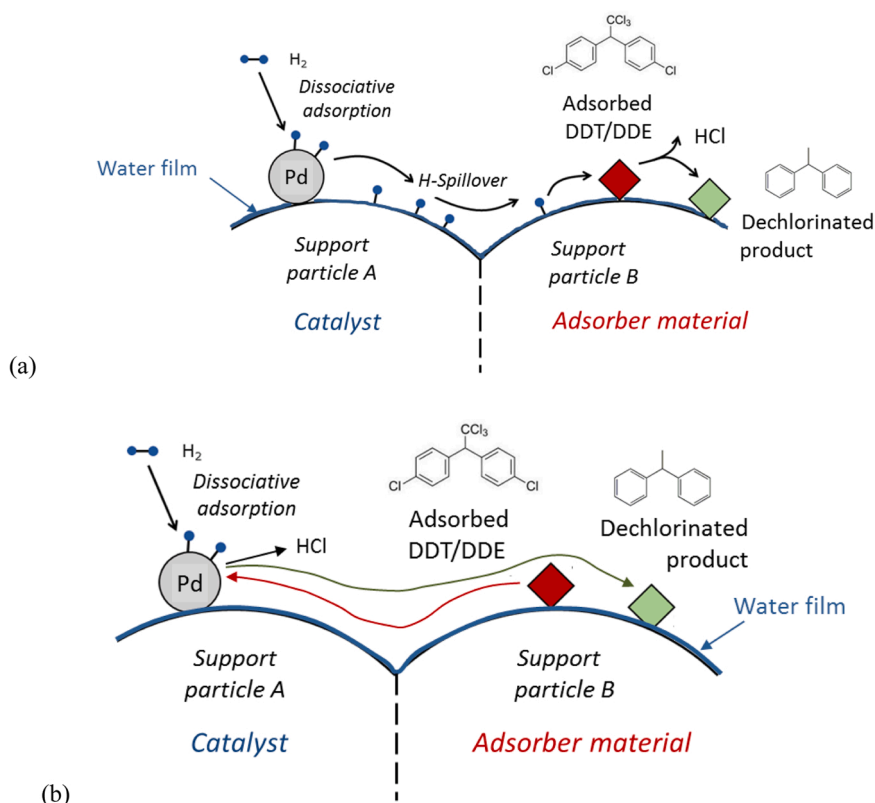


Fig. 1. Possible reaction pathways for the HDC reaction in two-component systems: (a) via hydrogen spillover and (b) long-distance migration of the (chlorinated) organic compounds at the water/gas phase interface.

surface, independent of its generation site. Different pathways would not be surprising, however, for reactions taking place at the metal surfaces [17,44,45]. This explanation requires diffusion of DDE (on silica of DDT) from the adsorption sites at the carrier surface to the metal clusters. There is, however, an alternative option to explain different product patterns by reactions with spilt-over H^* : the H^* surface concentration, which could be different for the Pd and Pt catalysts.

3.3. HDC under ambient conditions in one-component silica and activated carbon samples

Similar experiments were carried out with silica gel using both Pd and Pt as catalytically active metals (see Table 5). Immediately after preparation, the DHC to DDE was negligible; however, after storage for several days, a certain degree of DDE formation took place as observed in the reference samples.

Both catalysts contained 5 wt.-% of the active metal and had similar specific surface areas and metal dispersions (see Tables 2 and 3). Consistently, the mean distance between the metal clusters was relatively large with more than 500 nm. Table 5 shows the typical product patterns, comparable with those already discussed for alumina with a further hydrogenation of the aromatic rings when using Pt. Here, the presence of the intermediate product $Cy_2 > CH-CH_2Cl$ is remarkable. It may result from a stepwise HDC reaction (hydrogenolysis) at sp^3 -carbon in DDT or from a competition between hydrogenation and HDC at Pt sites. Any single Cl substituent at a sp^3 -carbon atom is less reactive towards further HDC [26,42].

A detailed analysis of the reaction pathways and their consequences in terms of products will be the subject of a further publication. For comparison with the oxide materials, a more hydrophobic Pd carrier based on activated carbon (AC) was used. There are a number of publications showing the H^* spillover on carbon surfaces [4,46,47].

As expected, a reference study without H_2 showed no conversion of

Table 5

Reactions of 0.5 wt.-% DDT impregnated on 5 wt.-% Pd on silica gel (Pd-K), on 5 wt.-% Pt on silica gel (Pt-M) and on 10 wt.-% Pd on AC (Pd-AC); gas flows 15 min N_2 , 5 h H_2 , 15 min N_2 , 25 mL min^{-1} each. As in the following tables, products with low molar contents are given as sum in the last line. The data are given in mole-% of the products in the sample extracts.

Catalyst	Pd-K		Pt-M		Pd-AC	
Reaction time in H_2 / h	0	2	0	2	0	5
DDT	92.6		68.9	2.7	98.0	32.7
DDE	6.9 *		29.8*			
$[Cl-Ph]_2 > CH-CH_3$						3.0
$[(Cl-Ph), Cy] > CH-CHCl_2$				2.1		
$Ph_2 > CH-CHCl_2$						2.2
$Cy_2 > CH-CH_2Cl$				23.2		
$Cy_2 > CH-CHCl_2$						2.9
$Cy_2 > C=O$		2.5				
$Ph_2 > C(OH)-CH_3$		4.3				
$Cy_2 > CH(OH)$				2.6		
$Ph_2 > CH-CH_3$		69.3				3.2
$[Ph, Cy] > CH-CH_3$		21.2				27.1
$Cy_2 > CH-CH_3$				64.1		20.2
Products < 2 mol-%	0.5	2.7	1.3	5.3	2.0	8.6
Recovery rate / % ⁺	130	100	98	61 **	86	56 **

* A slow DHC process was also observed for DDT-impregnated silica gel leading to some DDE formation after long storage times in the range of some weeks.

** Low recovery rates probably due to incomplete extraction or formation of non-extractable products.

⁺Amount of carbon extracted from the catalyst sample normalized to the initial carbon loading as DDT.

DDT including DHC to DDE. Preliminary experiments showed a relatively low reactivity of Pd/AC catalysts compared with alumina and silica systems having a similar Pd content. Therefore, the investigation was continued with 10 wt.-% Pd on AC and a reaction time of 5 h. Due to the large specific surface area of AC ($943 \text{ m}^2 \text{ g}^{-1}$), a highly disperse

Table 6

Reaction of DDE (from 0.5 wt.-% DDT) deposited on γ -Al₂O₃-A in a mixture with 0.5% Pd/ γ -Al₂O₃ (Pd-C) and with 5 wt.-% Pt/ γ -Al₂O₃ (Pt-H); gas flows 15 min N₂, H₂ purging time as stated, 15 min N₂, 100 mL min⁻¹ each. The data are given in mole-% of the products in the sample extracts.

Adsorber material	γ -Al ₂ O ₃ -A					γ -Al ₂ O ₃ -A	
Catalyst	Pd-C					Pt-H	
Reaction time in H ₂ / min	0	5	20	69	120	0	120
DDE	100.0	40.6	7.4	4.0		100.0	0.5
[Cl-Ph] ₂ >CH-CH ₃		1.6					4.3
[[Cl-Ph],Ph]>CH-CH ₃		1.3					
[[Cl-Ph],Cy]>CH-CH ₃							4.0
[Cl-Ph] ₂ >C=CHCl (DDMU)		2.3					
Ph ₂ >C(OH)-CH ₃		1.9	1.6	2.9	2.6		
Ph₂>CH-CH₃		51.7	86.5	87.7	90.6		
[Ph,Cy]>CH-CH ₃			1.3	2.5	3.9		1.6
Cy₂>CH-CH₃							89.7
Ph ₂ >C=CH ₂					1.2		
Products < 1 mol.-%		0.5	3.1	3.0	1.6		
Recovery rate / %⁺	89	83	90	94	98	29 *	91

⁺Amount of carbon extracted from the catalyst sample normalized to the initial carbon loading as DDT.

* Low recovery rate likely due to incomplete extraction.

distribution of DDT (0.5 wt.-%) could be expected. Despite the high Pd content, comparatively low reaction rates were nevertheless observed on AC as shown in Table 5. This may be due to a lower mobility of adsorbed DDT on the AC surface. Interestingly, the product spectrum is shifted towards a higher extent of hydrogenation to [Ph,Cy]>CH-CH₃ and Cy₂>CH-CH₃ than for Pd on oxidic carriers. The presence of compounds with residual chlorine both in the aliphatic (Cy₂>CH-CHCl₂ and Ph₂>CH-CHCl₂) as well as in the aromatic structure ([Cl-Ph]₂>CH-CH₃), together with the hydrogenation of the aromatic rings without prior full dechlorination of the aliphatic chain, could be an indication for different reaction competition, possibly affected by spilt-over H* species. The results show that the influence of the support is generally more pronounced than that of the metal loading (see also Supporting Information SI 5 for the influence of the metal content).

The main result of the studies with one-component samples is a fast and complete dechlorination of DDT and DDE under ambient conditions. The most plausible explanation is a certain mobility of the reactants DDT/DDE and/or H* on the catalyst surface, mediated by a thin water film under the experimental conditions applied.

In order to clarify the extent of surface mobility of DDT and related compounds in the context of the observed high reactivity at ambient temperature, further work was focused on two-component systems in which DDT and metals were placed on separate oxidic carrier particles. Here, diffusion lengths in the range of tens to hundreds of micrometers (particle sizes) rather than nanometers would be necessary for a chemical conversion of DDT/DDE.

3.4. HDC in two-component alumina samples

In a first set of experiments, metal-free γ -Al₂O₃-A impregnated with DDT was mechanically mixed with a catalyst Pd/ γ -Al₂O₃ (Pd-C, mass ratio 1:1, grain size fraction between 45 and 100 μ m). Surprisingly, as in the case of one-component systems described before, an almost complete dechlorination was observed within 2 h of hydrogen purging. A similar product pattern was found with at least 75% Ph₂>CH-CH₃ and the same minor products [Ph,Cy]>CH-CH₃, Ph₂>C=CH₂ and Ph₂>C(OH)-CH₃ (Supporting Information SI 2). As previously discussed, DDT appears as educt DDE due to initial HDC during the wet impregnation procedure. The two-step dechlorination pathway (first 1 atom from DHC, then 4 atoms from HDC) was confirmed by chloride analysis (0.97 and 4.08 moles chloride per mole of DDT, detected by means of IC).

It is interesting to note that the mean required diffusion distance of either DDE or H* to achieve chemical conversion is in the order of up to 50 μ m, including particle-particle interfaces. Nevertheless, the HDC reaction was almost complete. No chlorinated side products were found.

Residual DDE was the only chlorinated compound found after 2 h treatment in H₂.

As expected, the results were independent of the solvent for sample extraction when methanol was used instead of the toluene/chloroform mixture (Supporting Information SI 2).

The fast HDC and additional hydrogenation reaction of DDE can be illustrated by a set of experiments with variable hydrogen purging times summarized in Table 6. After only 5 min, more than 50% of DDE had been converted to Ph₂>CH-CH₃. After 20 min, only a small fraction of DDE remained. No DDE was found after 2 h. A slow hydrogenation of aromatic rings proceeded similarly to previous one-component experiments.

Similar experiments were carried out using DDT-impregnated particles with larger grain sizes (> 100 μ m). Under the same experimental conditions (2 h H₂, ambient temperature), significantly lower conversion rates (below 20%) were observed. As diffusion distances increased and assuming surface diffusion limitation of either activated H* species or chlorinated hydrocarbons, this was to be expected when postulating diffusion as one of several rate-determining steps. Both mechanisms are schematically represented in Fig. 1.

The product spectrum was comparable to previous experiments using Pd catalysts, with Ph₂>CH-CH₃ as main product. Again, only traces of partially chlorinated products were detected after hydrogen treatment.

In further experiments, the Pd/ γ -Al₂O₃ catalyst was replaced by one containing Pt (Pt-H). Mixing it with DDT impregnated on γ -Al₂O₃-A (grain size fraction 45–100 μ m) resulted in a high conversion of DDE to fully dechlorinated products after 2 h of H₂ purging (see also Table 6). Cy₂>CH-CH₃ was the main product rather than Ph₂>CH-CH₃, in conformity with results in the one-component systems, due to the higher hydrogenation activity of Pt compared to Pd.

When mixing Pt/ γ -Al₂O₃ with impregnated γ -Al₂O₃ (initial DDT content 0.5 wt.-%) in a ratio of 1:10 instead of 1:1, the conversion rate decreases due to the larger distance between metal clusters and contaminant. This is presented as a function of reaction time in Supporting Information SI 3. Besides the fully dechlorinated and hydrogenated product, Cy₂>CH-CH₃, considerable fractions of products with residual chlorine in the aromatic structure were found even after 4 h purging time. Apparently, the higher catalyst dilution (1:10) offers a sink for partially dechlorinated products, which eases back-diffusion away from the metal cluster. The observed product pattern (no aliphatic chlorines in one molecule with chlorine-free benzene rings) is in conformity with the reactivity pattern of Pt, which prefers aliphatic over aromatic chlorine substituents.

As in the case of Pd-containing systems, similar catalytic tests with

larger DDT/ γ -Al₂O₃ grains led to lower conversion rates but to similar product distribution.

3.5. HDC in two-component systems with silica gel

DDT remained stable on the surface of silica gel for several days after impregnation, as was confirmed by analysis of all reference samples without hydrogen purging. In experiments with only silica gel components and Pd catalyst (grain size 45–100 μ m, silica gel 60 and Pd-K), Ph₂>CH-CH₃ was also obtained as the main product (results not shown here). This means that DDT and DDE behave similarly with respect to HDC reaction.

Table 7 summarizes results from experiments where the DDT-impregnated silica particles were mixed with an inert component of silica gel and catalyst particles. The results give clear evidence of an interparticle long-range transfer of HDC reactivity, even for systems with a third blank particulate phase which has to be overcome by diffusion of either H* or DDT or both.

In order to check whether the lower observed conversion rates with the commercial Pd-K catalyst were caused by an incomplete activation, the catalyst was freshly activated in hydrogen at 400 °C for 4 h and an analogous experiment was carried out. However, no increase in conversion rates was found after this procedure, thus showing that the catalyst was already in the activated state in the previous experiments.

When Pd/SiO₂ (Pd-K) was substituted by a Pd/ γ -Al₂O₃ catalyst (Pd-C, grain size fraction 45–100 μ m), a much higher conversion was observed and almost no residual DDT was found when a 1:1 mixture was studied. The main product after 2 h hydrogen treatment was again Ph₂>CH-CH₃ (about 85%). A small amount of the hydrogenated product [Ph,Cy]>CH-CH₃ was also found (Table 7).

The tendency to higher reaction rates for alumina in comparison to silica support can be interpreted as an indication of a faster transport of H* or chlorinated hydrocarbons on the γ -Al₂O₃ surface. This includes the hypothesis that DDE formed in situ from DDT at the γ -Al₂O₃ surface could migrate faster than DDT itself. An explanation for the difference in surface mobilities could be the fact that DDE has a planar molecule structure, whereas the two aromatic rings in DDT are skewed. In plausible pictures: a flat molecule can possibly float better on a thin water film than a more bulky molecule.

The situation is different for experiments with Pt, e.g. a system consisting of DDT-impregnated silica gel, a Pt/ γ -Al₂O₃ catalyst (Pt-H) and inert porous silica (mechanical mixture with a mass ratio of 5:1:4). Here, after 2 h hydrogen purging a more diverse product pattern with

many partially chlorinated byproducts was observed (Table 7).

Beside the starting compound DDT and the final hydrogenation product Cy₂>CH-CH₃ typical for Pt-containing systems, several intermediate compounds were found. This could be favored by the presence of an inert component of pure porous silica, initially containing neither DDT nor a catalytically active metal (Pt). The silica surface seems to stabilize intermediate products which diffuse away from the metal sites after the reaction event. The bare silica particles may act as a kind of 'parking place' (sink) for intermediates after they have left the Pt clusters. There is a clear similarity to the function of inert alumina as sink of intermediates as discussed above and in Supporting Information SI 3 for diluted Pt/ γ -Al₂O₃.

Incomplete DDT conversion allows a more detailed analysis of the product spectrum. A first important finding is the presence of DDE, which is known to be formed by HDC on the γ -Al₂O₃, indicating that diffusion of DDT from silica to alumina takes place. This hypothesis is further supported by the formation of products probably originating from a pathway via DDE such as [Cl-Ph]₂>C=CHCl and [Cl-Ph]₂>C=CH₂. Here, HDC outcompetes hydrogenation. A second conclusion is that the dechlorination of the aliphatic chain is favored over that of the aromatic ring, which is also in agreement with results from the literature [26,42] and those to be presented in a forthcoming publication. The product spectrum also shows that hydrogenation of the aromatic rings can occur even when the dechlorination is not completed (e.g. presence of [Cl-Ph,Cy]>CH-CHCl₂ in combination with Cy₂>CH-CH₃). Apparently, hydrogenation can stabilize residual chlorine substituents, because C_{sp3}-Cl bonds such as in [Cl-Ph]₂>CH-CHCl₂ (DDD) and [Cl-Ph]₂>CH-CH₂Cl (DDMS) are less reactive towards HDC reaction than those in C_{sp2}-Cl bonds. Chlorinated cyclohexane rings were never observed, meaning that hydrogenation of benzene rings cannot outcompete HDC of chlorinated aromatics.

Further results with Pt-containing silica gel catalysts are presented in the Supporting Information part (SI 4).

3.6. Unsupported Pd micro-particles (μ -Pd) as catalyst for the HDC reaction

In order to eliminate the influence of catalyst supports, μ -Pd (grain size 1.2–2.5 μ m) was mixed intimately with non-porous α -Al₂O₃ resulting in a mean Pd concentration in the mixture of 1 wt.-%. This mixture was used as catalytically active component in combination with 0.5 wt.-% DDT on γ -Al₂O₃-A (grain size fraction 45–100 μ m). After standard hydrogen treatment, a DDE conversion of almost 60% was

Table 7

Reaction of 0.5 wt.-% DDT deposited on silica gel in a mixture with pure silica gel and a 5 wt.-% Pd-on-silica-gel catalyst (Pd-K), ratio 5:4:1, in a mixture with a 0.5 wt.-% Pd/ γ -Al₂O₃ catalyst (Pd-C), ratio 1:1, and in a mixture with pure silica gel and a 5 wt.-% Pt/ γ -Al₂O₃ catalyst (Pt-H), ratio 5:4:1 (gas flows 15 min N₂, H₂ purging time as stated, 15 min N₂, 100 mL min⁻¹ each). The data are given in mole-% of the products in the sample extracts.

Adsorber material	Silica gel								
Catalyst	Pd-K			Pd-C			Pt-H		
Reaction time in H ₂ / min	0	15	60	120	240	0	120	0	60
DDT	98.3	94.0	89.6	80.7	75.8	94.1	6.0	98.7	8.9
DDE	1.0					2.0			5.6
DDD		1.1				3.9	1.4		19.6
[Cl-Ph] ₂ >CH-CH ₃				1.3					6.9
[[Cl-Ph],Cy]>CH-CHCl ₂									4.9
[Cl-Ph] ₂ >C=CHCl									29.0
[[Cl-Ph],Ph]>CH-CHCl ₂									3.7
[Cl-Ph] ₂ >C=CH ₂									9.3
Cy ₂ >C=O							1.3		
Ph ₂ >C(OH)-CH ₃							1.3		
Ph ₂ >CH-CH ₃		3.9	10.4	15.3	19.4		84.9		
[Ph,Cy]>CH-CH ₃				1.4	3.3		3.9		
Cy ₂ >CH-CH ₃									11.2
Products < 1 mol-%	0.7	1.0		1.2	1.5		1.2	1.3	0.8
Recovery rate / % ⁺	75	75	69	78	67	84	93	135	99

⁺Amount of carbon extracted from the catalyst sample normalized to the initial carbon loading as DDT

Table 8

Reaction of DDE (from 0.5 wt.-% DDT impregnated on γ -Al₂O₃) in a mixture with μ -Pd and α -Al₂O₃ and reaction of crystalline DDT mixed with α -Al₂O₃ and a Pd/ γ -Al₂O₃ catalyst (Pd-D), ratio 1:1 (gas flows 15 min N₂, 2 h H₂ loading, 15 min N₂, 100 mL min⁻¹ each). The data are given in mole-% of the products in the sample extracts.

Adsorber material	γ -Al ₂ O ₃ -A		none	
Catalyst	μ -Pd		Pd-D	
Reaction time in H ₂ / h	0	2	0	2
DDT			99.4	6.6
DDE	100.0	41.2		3.9
DDD				8.5
[Cl-Ph] ₂ >CH-CH ₃		10.1		
Ph ₂ >CH-CH ₃		47.6		65.1
[Ph,Cy]>CH-CH ₃		1.1		10.4
Cy ₂ >CH-CH ₃				1.6
Products < 1 mol-%			0.6	3.8
Recovery rate / % ⁺	80	82	137	97

⁺Amount of carbon extracted from the catalyst sample normalized to the initial carbon loading as DDT

observed after 2 h as shown in Table 8. The reaction behavior of this three-component mixture was comparable with that of supported Pd catalysts, leading to the formation of Ph₂>CH-CH₃ as main product. The content of partially dechlorinated intermediates, namely [Cl-Ph]₂>CH-CH₃, was somewhat higher, which could probably be explained by the lower specific surface area of the Pd metal.

3.7. Reaction with crystalline DDT

The high HDC reactivity of DDT and DDE at ambient temperature that was observed even for two-component systems indicates a high surface mobility of either activated spillover hydrogen H* or chlorinated hydrocarbons with very low vapor pressures (namely with p_{DDT}^{20 °C} = 0.025 mPa [20]).

We were interested in the question of whether this reactivity/mobility is restricted to a highly dispersed state of DDT or is also valid for a crystalline DDT phase. Therefore, HDC experiments were carried out with crystalline DDT, which was initially comminuted (instead of impregnated from solution) with non-porous α -Al₂O₃. This powder was then mixed with a Pd/Al₂O₃ catalyst (Pd-D). Treatment for 2 h in hydrogen atmosphere led to the products shown in Table 8 (last column).

The result is comparable with that obtained for the impregnated DDT samples. Notably, some of the DDT did not react to DDE by DHC, which indicates that DDT was still present in a crystalline phase despite being mixed with γ -Al₂O₃. Interestingly, a conversion rate of more than 90% was achieved nevertheless after 2 h, which is similar to reactions with DDT impregnated on γ -Al₂O₃ (see Tables 4 and 6). Again, Ph₂>CH-CH₃ was the main product, and to some degree hydrogenation of aromatic structures occurred, leading to [Ph,Cy]>CH-CH₃. It is remarkable that the reaction mechanism of the well distributed DDT seems to be the same as for a pure crystalline DDT phase. [Cl-Ph]₂>CH-CHCl₂ (DDD), was found as intermediate product (8.5%) which is, in general, more typical for Pt catalysts. One can hypothesize that DDT is mobilized (it 'dissolves' on a surface) when its crystals come in close contact with a porous adsorber material such as γ -Al₂O₃.

3.8. Influence of the water content on the HDC reaction in two-component samples

As already discussed, the investigated samples usually exhibited the equilibrium water content after storage in ambient air. In order to study the influence of the sample moisture content explicitly, a set of experiments was carried out that is exemplarily discussed here for the two-component system with DDT-impregnated porous alumina (γ -Al₂O₃-A,

Table 9

Reaction of DDE (from 1 wt.-% DDT impregnated on γ -Al₂O₃-A) in a mixture with a Pt/ γ -Al₂O₃ catalyst (Pt-L), ratio 1:1 (gas flows 15 min N₂, 2 h H₂ with varying humidity, 15 min N₂, 100 mL min⁻¹ each). The data are given in mole-% of the products in the sample extracts.

Adsorber material	γ -Al ₂ O ₃ -A			
Catalyst	Pt-L			
Relative humidity of the gas flow / %	0	60	100	
Reaction time in H ₂ / h	0	2	2	2
DDE	100.0	89.9	9.3	
[[Cl-Ph],Ph]>CH-CHCl ₂		1.8		
Ph ₂ >C(OH)-CH ₃			6.4	28.0
Ph ₂ >CH-CH ₃			3.0	1.4
[Ph,Cy]>CH-CH ₃			4.8	4.2
Cy ₂ >CH-CH ₃		6.6	75.5	66.3
Products < 1 mol-%		1.7	1.0	0.2
Recovery rate / % ²	79	76	90	88

⁺Amount of carbon extracted from the catalyst sample normalized to the initial carbon loading as DDT

grain size fraction 45–100 μ m, DDT content 1 wt.-%) and a Pt/ γ -Al₂O₃ catalyst (Pt content 1 wt.-%, Pt-L) with a mass ratio of 1:1. During hydrogen treatment, the humidity of the purge gas stream (100 mL min⁻¹) was established to a defined water concentration using a salt-containing water bath. As shown in Table 9, the conversion was strongly dependent on the water content of the sample. Whereas the rate was relatively low for a dry gas stream leading to an ongoing desiccation of the sample, moist purge gas streams had high conversion rates leading to the expected products when using Pt catalysts. Interestingly, there seems to be an optimum for mean water contents showing the highest yield of fully dechlorinated and hydrogenated product Cy₂>CH-CH₃. Although the extent of oxidation during extraction obviously varied, the product Ph₂>C(OH)-CH₃ is an indication for the precursor Ph₂>CH-CH₃ rather than Cy₂>CH-CH₃. This hypothesis is in conformity with the much higher reactivity of the tertiary C-H bond in the aromatic compound.

The strong influence of the sample moisture could be explained by two different phenomena: (i) the known influence of water on the H* spillover and especially the primary spillover step, i.e. the transfer from the metal onto the support [4,48,49]; however, it can also be considered as a strong indication for (ii) the role of water films for the migration of contaminants inside the porous samples as main mechanism allowing the long-range reactivity especially in the two-component samples. The occurrence of an optimum in water content is probably due to the pore-filling at higher purge gas humidities hindering the migration of the hydrophobic, poorly water-soluble compounds. This is supported by the fact that the estimated water contents in the alumina samples corresponded to sub-monolayer water coverage when considering the determined specific surface areas (see Table 2).

4. Summary and Conclusions

A long-range catalytic hydrodechlorination (HDC) combined with partial or complete hydrogenation was shown with DDT as a model substance of high relevance as an environmental contaminant. Porous γ -alumina as adsorbent and catalyst support led to a fast transformation of DDT to DDE by a dehydrochlorination (DHC) reaction, most probably correlated with the presence of basic surface sites. The reactions took place even when DDT or DDE and the metal component were deposited separately on different particles. The reactions proceeded already at ambient temperature and in granular fixed-bed samples having equilibrium moisture content after storage at ambient air. The course of chemical reactions requires interactions between DDT or DDE and the metal component over a distance of up to hundreds of micrometers. This interaction can either be due to a diffusion of activated H* species (hydrogen spillover) or a surprisingly high mobility of DDT and DDE on

the surface of the carrier materials. High or even complete conversion was observed within a few hours or even within several minutes. Because a migration of both H^* or DDT and DDE via the gas phase is unlikely, a fast transfer across surfaces and grain boundaries in mechanical mixtures obviously takes place.

The reactivity in samples with a certain water content was higher than that of dry samples. Therefore, water films appear to play an important role in the transport of reactants. Although a positive influence of water on the transfer of H^* to the support (primary spillover step) has been described in literature [4,48,49], a fast migration of DDT and DDE on the surface of water films is the most plausible interpretation of the experimental results [50]. This diffusion at the boundary between water and gas phase should be the preferred transport mechanism in contrast to the diffusion inside a water multilayer structure, due to the very low water solubilities of DDT ($1.2\text{--}5\text{ }\mu\text{g L}^{-1}$ at $20\text{ }^\circ\text{C}$) and DDE ($10\text{--}120\text{ }\mu\text{g L}^{-1}$ at $20\text{ }^\circ\text{C}$ [32,66]), and also when compared to diffusion at the dry surface due to the strong adsorption.

It is noteworthy that an effective HDC reaction including long-range diffusion is also found for high DDT loadings and even for crystalline DDT in combination with various supported catalysts. Additionally, the feasibility of unsupported metal as microparticles was also shown.

A strong indication for the migration of DDT or DDE as the dominating process for bridging adsorption and catalytic sites is the observed reaction selectivity when comparing Pd and Pt as metal components. In agreement with results from the literature [44,45], Pt is more active with respect to the hydrogenation step occurring in addition to dechlorination. Therefore, $\text{Cy}_2\text{>CH-CH}_3$ is the main product with Pt catalysts whereas $\text{Ph}_2\text{>CH-CH}_3$ is preferentially formed in Pd-containing systems. In contrast, the nature of activated H^* spillover species should be the same for both catalysts [5,6] and only their local concentration could vary. However, the described selectivity was observed for various experimental conditions; therefore, an interpretation based on varying H^* concentrations is considered less plausible.

Analyzing various impregnated adsorbents and catalysts with different activities for DHC reactions also showed a significant influence of the hydrophobicity on the long-range catalytic process. The mobility of the contaminants on activated carbon is relatively low. This is in agreement with the image that aromatic hydrocarbon molecules remain adsorbed on the carbon surface, even in the presence of water films. The migration is faster on more hydrophilic oxide supports such as $\gamma\text{-Al}_2\text{O}_3$, silica gel or also other metal oxides, the latter not presented explicitly in this study. This supports the image that the hydrophobic molecules 'swim' on a more-or-less closed water film which covers the oxide surface.

Since, for all these materials, spillover of H^* species has previously been described [4–6], additional reaction pathways via H^* spillover and a reaction taking place at the surface of the support cannot be excluded. This hypothesis is supported by comparing product selectivities with respect to intermediates of the HDC of DDT in aqueous phase with unsupported metal catalysts (colloids) and HDC in the systems used in this study. A more detailed analysis will be made in a forthcoming paper.

Remote control in catalysis and even synergistic catalytic functions have been found for many processes in heterogeneous catalysis (bifunctional catalysis, selective oxidation, hydrogen and oxygen spillover [1–9]). Here, another long-range interaction was found in the context of HDC reactions. It is probably based primarily on the high mobility of practically non-volatile and non-water-soluble DDT and DDE at the surface of water films. However, H^* spillover and reaction steps on the surface could also contribute to some reaction pathways.

The results of this study are not only relevant from the mechanistic point of view (long-range action, interplay of dechlorination and hydrogenation, comparison of the reactivity of aliphatic and aromatic chlorine substituents in one molecule, influence of the support material). There are also some possible applications for destruction of chlorinated organic contaminants often used as biocides in the context of regeneration of spent adsorbents and filters as well as decontamination

of wooden structures and artwork treated with timber preservatives. Target compounds other than DDT, such as lindane or pentachlorophenol, were already shown to be accessible in this way.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

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